AUTOCATALYTIC LIQUEFACTION OF COAL

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INTRODUCTION

In coal liquefaction, conversion of solid coal to a liquid takes place in a step-wise manner, essentially in two stages. In the first stage, pyrolitic break-up of the coal matrix takes place under mild conditions of temperature and pressure at short reaction times[1-4] yielding a highly viscous intermediate product containing mostly asphaltenes. The initial pyrolitic reaction is fast and does not need any catalyst. In the second stage, the intermediate product undergoes a series of cracking and hydrogenation reactions and is converted to a refined oil. The second stage conversion requires relatively severe conditions of temperature and pressure, longer reaction times and an effective catalyst.

In most of the coal liquefaction processes (SRC[5], EDS[6], H-Coal[7]) under development, conversion of coal to the liquid product takes place in a single step operation. Coal liquefaction and upgrading of the liquefied coal take place under the same conditions and in the same reactor. But it is advantageous to carry out coal liquefaction in two separate steps because each step can be carried out under conditions optimal for it. The two-step approach was used in some of the German plants[8] where coal paste was hydrogenated in the first step and the middle oil fraction of the product was hydrocracked to gasoline in a second step. The CSF process[9] developed by the Consolidation Coal Company was also carried out in two separate steps. In the first step, a coal extract was produced which was subsequently hydrocracked in a second step to gasoline using molten zinc chloride as the catalyst. At the present time, a two-step liquefaction process[10,11] is being developed under the joint sponsorship of the U.S. Department of Energy, The Lummus Company and Cities Service Research and Development Company for the production of distillate oil from coal. In this process, coal undergoes liquefaction at short reaction times in the first step and the liquefied coal, after removal of the solids, undergoes catalytic hydrocracking in the second step. The hydrocracking takes place in an expanded bed reactor using a commercial nickel-molybdenum catalyst. It was claimed that the two-step operation increases liquid product yield and improves hydrogen utilization efficiency. This paper describes the development of the Autocatalytic Coal Liquefaction process which also operates in two steps. In the first step, coal undergoes liquefaction at short reaction times and the liquefied coal undergoes catalytic hydrocracking in the presence of a coal derived mineral catalyst in the second step.

EXPERIMENTAL

A bituminous coal blend made out of Kentucky No. 6 and No. 11 coals was used in the Short Reaction Time (SRT) liquefaction experiments. The analysis of the blended coal is given in Table 1. A distillate coal liquid produced from the blended coal at the Wilsonville coal liquefaction pilot plant was used as the solvent in the SRT liquefaction experiments. The analysis of the solvent is given in Table 2. The hydrogen content of 8.18 percent and a H/C (atomic) ratio of 1.12 indicate that the solvent contains a fairly high concentration of hydroaromatics. The SRT liquefied coal used as the feed in the hydrocracking experiments was prepared in a batch stirred autoclave from the blended coal using the Wilsonville solvent at 450°C, 2500 psi and 10 minutes reaction time. The analysis of the SRT liquefied coal is given in Table 3. It contains about 68 percent solvent and 7.3 percent solids. The coal mineral catalysts used in this work were also produced at the Wilsonville pilot plant by filtration and Kerr-McGee deashing processes. The raw catalysts were cleaned by hydrotreatment in the presence of the Wilsonville solvent under hydrogen pressure in an autoclave, washed with THF and ground to -200 mesh before use. The analysis of the catalysts is given in Table 4. The pyrrhotite content was calculated from the Fe_2O_3 content of the ash. The blended coal, solvent, and coal mineral catalysts were obtained from the Southern Company Services, Inc., Birmingham, Alabama.

The SRT coal liquefaction and the hydrocracking experiments were carried out in a batch stirred autoclave assembly shown in Figure 1. The magnedrive autoclave was supplied by the Autoclave Engineers, Erie, Pennsylvania. Two high pressure feeders were added to the autoclave to feed coal slurry into the hot autoclave. The autoclave was flushed with nitrogen, pressurized with hydrogen and heated to about 550°C. In the SRT liquefaction experiments, about 100 grams of coal was mixed with about 200 grams of the solvent and the catalyst. The slurry was then fed to the hot autoclave through the feeders. In the hydrocracking experiments, the liquefied coal was mixed with the coal mineral catalyst and the slurry was fed to the hot autoclave. After the feed was fed to the autoclave, the temperature and pressure of the autoclave were adjusted to the desired reaction conditions. Reaction was carried out for a predetermined length of time, the contents of the autoclave were cooled and the products were withdrawn. The solids were separated from the liquid product by high pressure filtration. The analyses of gas, liquid and solid products were done by standard methods. The following definitions are used in this paper.

Preasphaltene:	product soluble in THF but insoluble in benzene
Asphaltene:	product soluble in benzene but insoluble in hexane
Residue:	product insoluble in THF

RESULTS AND DISCUSSION

Coal Liquefaction

Conversion of coal to soluble liquid products takes place at moderate temperatures and short reaction times in the presence of a hydrogen donor solvent and molecular hydrogen. Under mild conditions, the coal matrix undergoes thermal break-up and form reactive fragments which extract hydrogen and become stable compounds. The optimal conversion of coal to stable compounds depends upon the temperature, reaction time, hydrogen pressure, solvent quality and catalyst. In the present work, the influence of temperature, pressure, reaction time and catalyst on coal liquefaction was investigated in the presence of a coal derived solvent.

The effect of temperature is shown in Figure 2. The total conversion of coal increased from 69-91 percent when the temperature increased from 430-460°C at ten minutes reaction time. As can be expected, the yield of gas has increased and the residue decreased with total conversion. But the liquid product yield peaked at 450°C and showed a declining trend as the temperature increased to 460°C. The data of Figure 2 therefore suggest that a temperature of 450°C is optimal for obtaining maximum liquid product at a short reaction time of ten minutes and a pressure of 2500 psi. The liquid product yield under these conditions was 71 percent of the daf coal.

The effect of reaction time and catalyst on conversion is shown in Figure 3. The coal conversion increased with reaction time in all cases. In the noncatalytic case, conversion increased faster in the first seven minutes but slowed down at longer times. But in catalytic conversion, there was a steady increase in conversion with reaction time. The data of Figure 3 show that the addition of catalyst improved the conversion but the improvement was not very significant up to ten minutes reaction time. Even at longer times, the improvement in conversion did not exceed 5 percent. It can therefore be inferred from the data that the addition of coal mineral catalyst does not improve coal conversion to any significant extent during the initial depolymerization of coal to soluble products at short reaction times.

The effect of pressure and reaction time on conversion is shown in Figure 4. The coal conversion increased with both pressure and reaction time. The effect of pressure on conversion was not significant, especially between 2500-2800 psi and a pressure of 2500 psi appears to be optimal for this step. The conversion improved by 6-7 percent when the pressure increased from 2100-2500 psi and only by about 2 percent when the pressure increased from 2500-2800 psi.

An examination of the liquid products obtained at different reaction times revealed that the product becomes more reactive when the reaction time exceeds seven minutes. The liquefied coal products obtained at 3, 7 and 12 minutes reaction time were subjected to autocatalytic hydrocracking to find out their reactivities. The data of Table 5 show that the conversion of hexane insolubles (preasphaltene and asphaltene) and removal of sulfur and nitrogen increased in the order 12 minute liquid >7 minute liquid >3 minute liquid. The increase in the conversion of the 7 minute liquid over the 3 minute liquid was small but the conversion of the 12 minute liquid showed a large increase over the 7 minute liquid which indicates that the reactivity of the liquefied coal increases with the reaction time of liquefaction and the liquid becomes more amenable to the action of the catalyst.

It is concluded from the foregoing discussion that the initial coal liquefaction step is fast and does not need any external catalyst. The reactivity of the liquefied coal increases with liquefaction time and the products obtained at reaction times of 12 minutes or longer will be amenable to the action of the coal mineral catalyst.

Hydrocracking of Liquefied Coal

The short reaction time (SRT) liquefied coal (Table 3) was hydrocracked at 460°C, 2500 psi and 30 minutes reaction time with different concentrations of the coal mineral catalyst. The effect of catalyst concentration on the yield of liquid, solid and gaseous products is shown in Figure 5. The yield of liquid product decreased from 75 to 70 percent with an increase in the catalyst concentration which indicates that the hydrocracking of SRT liquefied coal increases with catalyst concentration. The gradual decrease in the yield of solid product indicates that some of the insoluble organic matter present in the feed undergoes conversion during hydrocracking. It also indicates that coke formation does not take place during hydrocracking under the experimental conditions used. The increase in gas yield appears to be due to the increase in the hydrocracking conversion of the liquefied coal.

The quality of the liquid product improved with an increase in the concentration of the coal mineral catalyst as shown in Figure 6. The hexane insolubles (preasphaltenes and asphaltenes), sulfur and nitrogen contents of the product decreased, resulting in the production of a good quality product, especially at a catalyst concentration of 25 percent. The properties of the liquid product given in Table 6 show that more than 90 percent is distillable and it contains substantial quantities of light and middle oils.

It is concluded from the hydrocracking data that the SRT liquefied coal can be hydrocracked to a refined distillate oil using high concentrations of the mineral residue as the catalyst. More than 50 percent of the organic insolubles also undergo conversion during hydrocracking.

Autocatalytic Liquefaction Process

The work described in the foregoing sections led to the evolution of the JPL Autocatalytic Coal Liquefaction process shown in Figures 7 and 8. The process has two basic steps as shown in Figure 7. In the first step, coal undergoes liquefaction under high temperatures and pressures at short reaction times. In the second step, the product of the first step which contains liquefied coal, unconverted coal and coal minerals undergoes hydrocracking in the presence of a coal mineral catalyst in high concentrations of about 25 percent producing a refined distillable product.

The material balance of the autocatalytic liquefaction process given in Table 7 shows that the process produces a distillate product in a yield of 67 percent at a hydrogen consumption of 4.5 percent. Based on the bench scale data, a conceptual flow diagram of the process was developed as shown in Figure 8. In this process scheme, part of the filter cake (mineral catalyst) is recycled to the hydrocracker and the solids are separated from the product by filtration. The process produces a low viscosity lighter product which filters easily. The hydrogen for the process is produced by the reforming of a mixture of coal gas produced in the process and natural gas obtained from an external source.

ACKNOWLEDGEMENT

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Table 1. COAL ANALYSIS

		BITUMINOUS (KENTUCKY #6 AND #11)
PROXIMATE ANALYSIS, WT.% (Dry Basis)		
Volatiles	:	46.43
Fixed Carbon	:	44.17
Ash	:	9.40
ULTIMATE ANALYSIS, WT.% (Dry Basis)		
Carbon	:	73.44
Hydrogen	:	5.30
Nitrogen	:	1.21
Sulfur	:	3.35
Oxygen (By difference)	:	7.30
Ash	:	9.40
$H/_C$ (Atomic)	:	0.87
size	:	70%, - 200 Mesh

Table 2. ANALYSIS OF SOLVENT

Sp. gr., 25°C	:	1.040

DISTILLATION DATA, °C%

I.B.P.	:	130
50% B.P.	:	300
90% B.P.	:	400
E.B.P.	:	430
Preasphaltene, Wt.%	:	11.0
Asphaltene, Wt.%	:	17.0

ELEMENTAL ANALYSIS, WT.%

Carbon	:	87.80
Hydrogen	:	8.18
Nitrogen	:	1.02
Sulfur	:	0.48
Oxygen (By difference)	:	2.52
$H/_C$ (atomic)	:	1.12

Table 3. ANALYSIS OF SHORT REACTION TIME (SRT) LIQUEFIED COAL

RAW FEED

Total Solids, Wt.% (THF insolubles)	:	7.3
Solvent, Wt.%	:	67.7
Liquefied Coal, Wt.%	:	25.0

FILTERED FEED

Viscosity, Cps at 150°C	:	310
Preasphaltene, Wt.%	:	21.0
Asphaltene, Wt.%	:	20.0
Sulfur, Wt.%	:	0.91
Nitrogen, Wt.%	:	1.20
Carbon, Wt.%	:	87.1
Hydrogen, Wt.%	:	7.71
Oxygen, Wt.% (By difference)	:	4.23
$H/_C$ (atomic)	:	1.06

Table 4. ANALYSIS OF CATALYSTS

	MINERAL RESIDUE	
	FILTER CAKE	ASH CONCENTRATE
Total Solids, Wt.% (THF insolubles)	100.0	100.0
Ash, Wt.%	79.14	-
Carbon, Wt.%	10.50	-
Hydrogen, Wt.%	0.61	-
Sulfur, Wt.%	0.54	-
Nitrogen, Wt.%	0.20	-
Oxygen Wt.% (By calculation)	11	-
$H/_C$ (atomic)	0.70	-
Pyrrhotite, Wt.%	30.9	-
Size	-200 mesh	-200 mesh

TABLE 5. AUTOCATALYTIC HYDROCRACKING OF SRT LIQUEFIED COAL OBTAINED AT DIFFERENT REACTION TIMES

Temperature	:	460°C
Reaction Time	:	20 min.
Pressure	:	2500 psi
Catalyst	:	25% Wt.

	Feed		
	3 min. Coal liquid	7 min. Coal liquid	12 min. Coal liquid
Conversion of Hexane Insolubles, Wt.%	8.5	11.5	47.0
Sulfur removal, Wt.%	12.0	14.5	39.5
Nitrogen removal, Wt.%	7.4	10.2	25.6

TABLE 6. PROPERTIES OF COAL LIQUID PRODUCED BY SHORT REACTION TIME AUTOCATALYTIC COAL LIQUEFACTION

Sp. gr. at 25°C	:	1.05

<u>Distillate Data, °C</u>

I.B.P.	:	65
50% B.P.	:	315
90% B.P.	:	425

<u>Elemental Analysis, Wt.%</u>

Carbon	:	86.80
Hydrogen	:	9.63
Nitrogen	:	0.92
Sulfur	:	0.31
Oxygen (By difference)	:	2.34
H/C (Atomic)	:	1.33
Hexane Insolubles, Wt.%	:	7.8

TABLE 7. NORMALIZED MATERIAL BALANCE OF SRT AUTOCATALYTIC LIQUEFACTION OF COAL (DRY COAL BASIS).

<u>INPUT, g</u>

Coal	:	100.0
Solvent	:	200.0
Hydrogen	:	4.5
Catalyst	:	79.0
Total	:	383.5

<u>OUTPUT, g</u>

Gas (includes H_2S and NH_3)	:	17.0
Water	:	4.8
Coal Liquid	:	67.0
Solvent	:	200.0
Residue	:	94.7

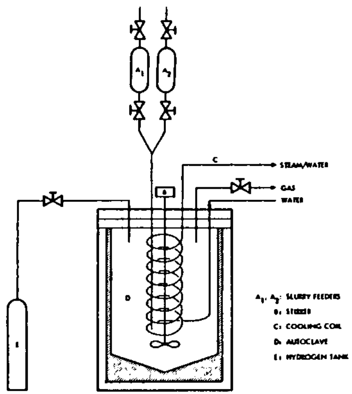

FIGURE 1: BATCH AUTOCLAVE ASSEMBLY

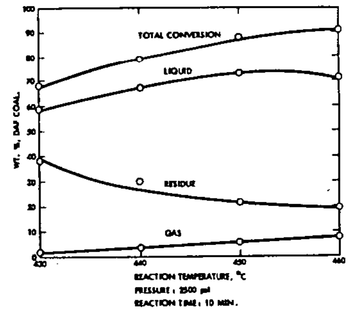

FIGURE 2: EFFECT OF TEMPERATURE ON COAL LIQUEFACTION

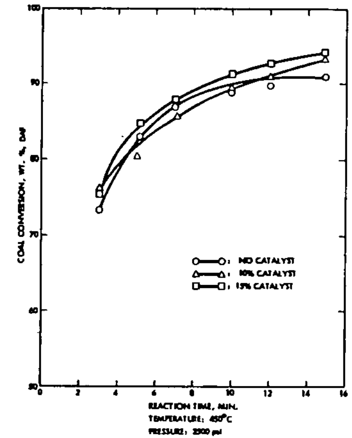

FIGURE 3: EFFECT OF REACTION TIME AND CATALYST ON COAL LIQUEFACTION

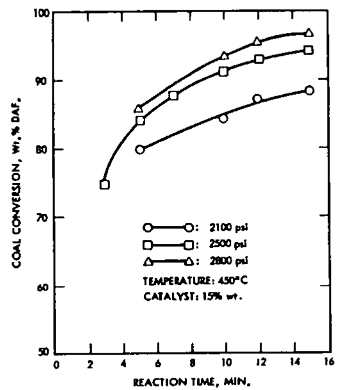

FIGURE 4. EFFECT OF PRESSURE AND REACTION TIME ON COAL CONVERSION

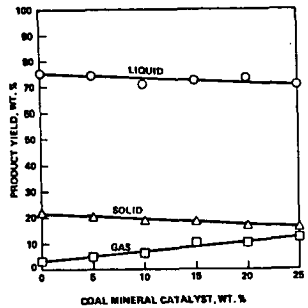

FIGURE 5. EFFECT OF CATALYST CONCENTRATION ON PRODUCT YIELD

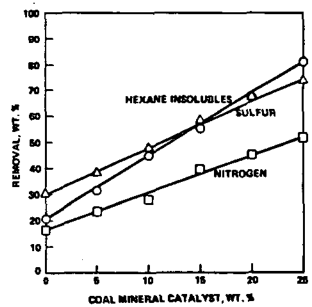

FIGURE 6. EFFECT OF CATALYST CONCENTRATION ON PRODUCT QUALITY

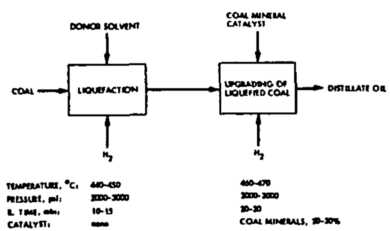

FIGURE 7. TWO-STEP COAL LIQUEFACTION CONCEPT

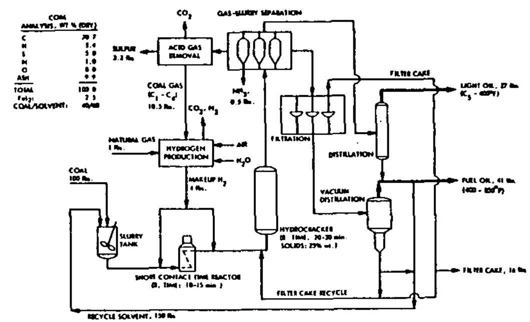

FIGURE 8. CONCEPTUAL FLOW DIAGRAM OF THE AUTOCATALYTIC COAL LIQUEFACTION PROCESS